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AIR EMISSIONS FROM INDUSTRIAL BOILERS BURNING HAZARDOUS WASTE MATERIALS

by

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16. ABSTRACT

Hazardous waste incinerators are tightly regulated under the Resource Conservation and Recovery Act (RCRA). On the other hand, processes for which the primary purpose is production of energy but, incidentally, burning hazardous wastes are exempt from the RCRA incineration regulations. EPA is concerned about the impact of this "Energy Exemption" and has initiated a test program to determine if and to what extent regulation of such processes may be required. The most significant practice that currently is excluded from regulation is disposal of hazardous materials in industrial boilers. There are currently in the U.S. approximately 240,000 operating industrial boilers and a large percentage of these boilers are accessible to hazardous wastes. This paper describes the testing of 12 such industrial boilers of various types using varying waste materials and test "spiked" materials. Test site selection is discussed, sampling and analytical methodologies are presented and test results are summarized. The primary focus of the test program was on the ability of the boilers to destroy principal organic hazardous compounds (POHCs) and also to characterize and quantify emissions of products of incomplete combustion (PICs). Measurements of particulate emissions, CO, NO_x, and THC were also recorded. Attempts were made to establish correlations between boiler type, boiler operating parameters and waste destruction efficiencies.

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ASTRACT

The performance of hazardous waste incineration is regulated under the Resource Conservation and Recovery Act (RCRA). Industrial processes for which the primary purpose is production of energy but incidentally, burn hazardous wastes are exempt from compliance with the RCRA incineration regulations. EPA is concerned about the impact of this "energy exemption" and has initiated a test program to determine if and to what extent regulation of such processes may be required. The program includes testing of industrial boilers, industrial kilns, steel mills, and other industrial processes. This paper discusses the boiler test program. Results of four boiler tests are presented. Data on emissions of organic hazardous materials as well as criteria pollutants are provided. Boiler operating parameters that may impact emissions are discussed.

INTRODUCTION

EPA's regulations for incineration of hazardous wastes require that incinerators must achieve a Destruction and Removal Efficiency (DRE) of at least 99.99 percent of the Principal Organic Hazardous Constituents (POHCs) present in the waste. Processes that primarily produce energy and incidentally burn hazardous wastes are currently exempt from the hazardous waste destruction performance regulations that apply to incinerators. These exempted processes include industrial boilers, kilns, and other industrial thermal processes, such as furnaces and ovens.

Even though industrial processes that burn hazardous wastes are exempt from incinerator regulations, EPA is conducting an investigation into the need for regulating such practices. Of particular concern are industrial boiler since there are over 240,000 such units in the United States, many of which have access to one or more of the 450 listed RCRA hazardous wastes.[1] A part of this investigation of boiler disposal of hazardous waste materials is a Regulatory Impact Analysis (RIA) which includes both technical and economic analyses.

This paper presents and discusses data obtained from four full-scale tests conducted by EPA. The test subjects were industrial boilers that burned hazardous waste materials in conjunction with a primary fossil fuel.

MEASURES OF PERFORMANCE

While industrial boilers are not currently regulated under the Resource Conservation and Recovery Act (RCRA) it is appropriate that their performance as hazardous waste material disposal systems be measured against EPA's incineration regulations. Specifically, these regulations for organic waste destruction are:[2]

$$DRE = \frac{Win - Wout}{Win} \times 100 \geq 99.99 \text{ percent}$$

where

Win = Mass flowrate of a POHC in the waste fuel.
Wout = Stack emission rate of a POHC.

In addition, emissions of criteria pollutants such as carbon monoxide (CO), oxides of nitrogen (NO_x), hydrocarbon (HC), and particulate matter are important measures of combustion performance acceptability and correlation of these parameters with organic waste destruction efficiency is a major goal of EPA's research into hazardous waste combustion. Since many hazardous waste compounds are chlorinated materials, emissions of hydrochloric acid (HCl), which are regulated under the RCRA incinerator regulations, are also measurement targets.

SAMPLING AND ANALYTICAL PROTOCOLS

The sampling requirements for waste combustion testing were sufficiently complex that three separate stack sampling trains were used. Continuous monitors with strip chart recorders were used for gaseous emission species measurements. In addition, extensive periodic waste and primary fuel sampling

was required. While subtle variations in protocol were required to accommodate differing site and waste characteristics, the sampling and analytical procedures were basically as follows.

The Modified EPA Method 5 train was used to collect semivolatile organics (boiling point >100°C) and particulate matter. The semivolatile materials were collected on XAD-2 resin that was analyzed for POHC material by GC/MS. Figure 1 is a schematic of the Volatile Organic Sampling Train (VOST) that was used to collect volatile organics for subsequent GC/MS analysis.[3] The heart of this train consists of two resin traps in series. The first resin trap contains TENAX and the second resin trap contains TENAX with an activated charcoal backup. The Method 6 train was used to sample for HCl emissions. Analysis was conducted by titration of the impinger liquid using a standard solution of silver nitrate.

Table I describes the continuous monitoring equipment used to record gaseous emissions. C_1 through C_6 hydrocarbons were collected in a stainless steel cylinder and analyzed in an onsite gas chromatograph. Waste and fuel samples were collected at half-hour intervals and composited. The composited samples were analyzed by GC/Hall and GC/FID for POHCs and for total chlorides, C,H,N,O,S, and HHV by ultimate analysis ASTM methods.

For all tests, trip and field blanks were used for the resin cartridges. In addition, laboratory blanks were used to ascertain the absence of laboratory contamination. For each test series, background tests were conducted with the primary fossil fuel alone (no hazardous waste materials).

For most tests, waste materials of particular interest were "spiked" (added) to the waste material normally burned to facilitate data interpretation and to allow comparison across the combustor types. The spike materials usually consisted of chlorinated organic materials such as carbon tetrachloride, 1,1,2 trichloroethylene, and chlorobenzene. The spike materials were chosen because they were suspected to be more thermally stable than the nonhalogenated organics usually encountered in boiler co-firing operations. Also, the spike compounds represented a range of volatilities to facilitate comparison of the Modified Method 5 and VOST sampling trains.

TESTS DESCRIPTIONS

The four tests described here were conducted as part of a 12-test series of full-scale boiler tests to support EPA's Regulatory Impact Analysis (RIA) effort for industrial boilers. For the sake of brevity, the test descriptions will be greatly condensed and not all data from all test sets conducted at each test site will be described. In return for their participation in this voluntary test program, each boiler site has been guaranteed anonymity so the boilers will only be identified by numbers.

Boiler Number One

Industrial boiler number one was a forced draft packaged watertube A-type Combustion Engineering boiler. Its maximum steam load capacity was 13.9 kg/s (110,000 lb/hr)of superheated steam at 2.94 MPA (425 psig) and 315°C (600°F). The unit, installed in 1971, was equipped with one dual air

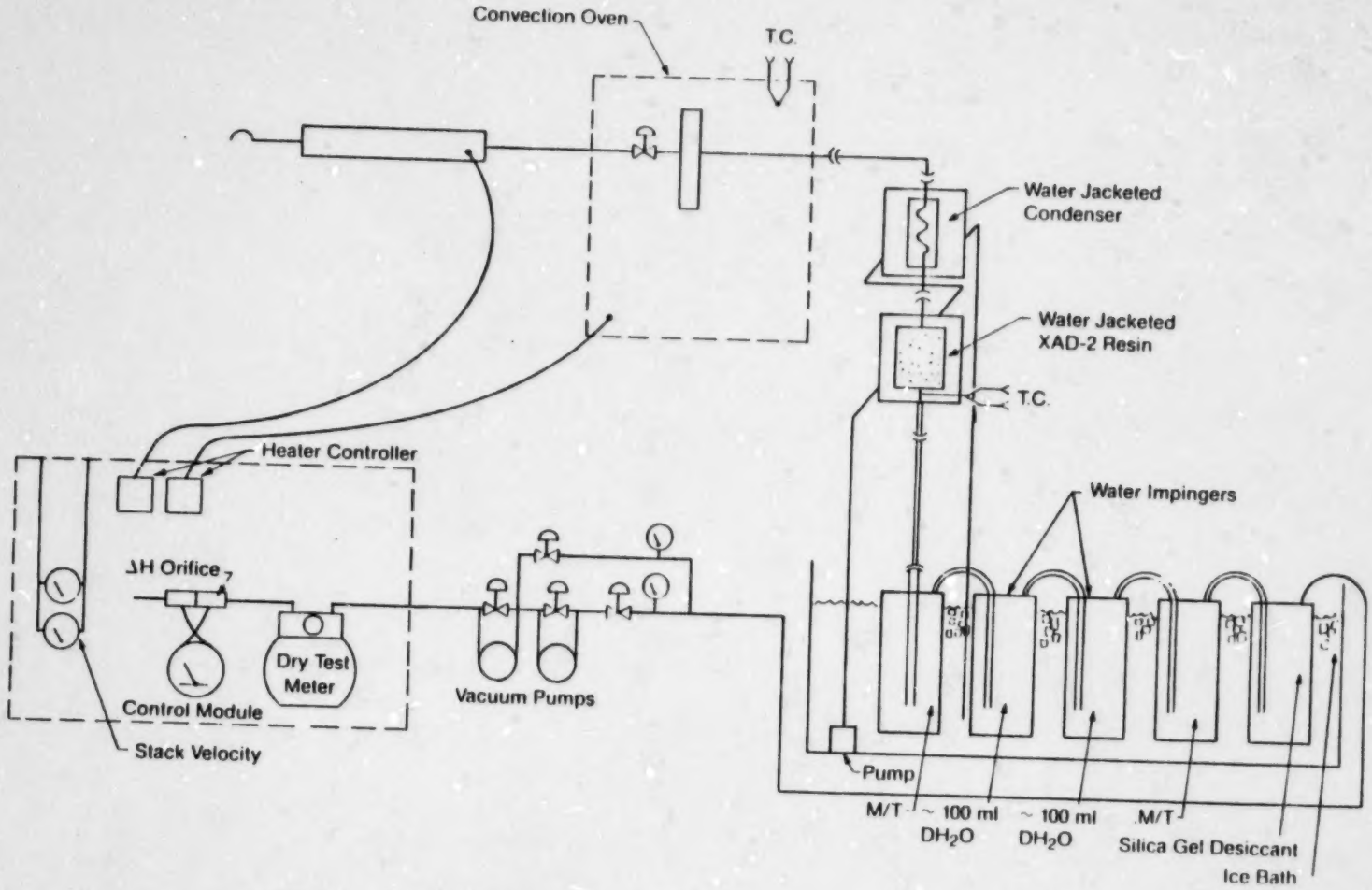

FIGURE 1 - Modified EPA Method 5 Train

register gas and oil fired COEN burner. The furnace had a volume of 41.9 m^3 (1480 ft^3) and a heating surface of 665 m^2 (7158 ft^2) providing volumetric and surface heat release rates of 862 KW/m^3 (81,700 Btu/hr ft^3) and 52.7 KW/m^2 (16,950 Btu/hr ft^2) respectively at maximum heat input capacity. Combustion air was not preheated and the flue gas was not treated for particulate control. Typical operating steam load was approximately 6.3 kg/s (50,000 lb/hr).

TABLE I - CONTINUOUS MONITORING EQUIPMENT

Instrument	Principal of Operation	Manufacturer	Instrument Model
NO_x	Chemiluminescence	Thermo Electron	10 AR
CO	Nondispersive infrared (NDIR)	ANARAD	500R
CO_2	Nondispersive infrared (NDIR)	ANARAD	AR500
O_2	Fuel cell	Teledyne	Not Available
Total HC	Flame ionization detector (FID)	Beckman	400
Sample gas conditioner	Refrigerant dryer-condenser	Hankinson	E-4G-SS
Strip chart	Dual-pen analog	Linear	400

The boiler was retrofitted to fire organic wastes produced at the site. Waste fuel was injected through two guns located on either side of the center fuel oil gun. Each waste gun tip had three nozzles positioned such that the waste fuel spray was diverted away from the main fuel oil spray. Both oil and wastes were steam atomized.

The testing described here consisted of three series of tests, including one baseline test and two sets of cofiring tests. The baseline fuel was No. 6 oil. During the second series of tests, heat input from the No. 6 oil was supplemented with the waste fuel available at the site. This waste, a process production bottom, contained methyl methacrylate (MMA) as the POHC of interest. During the third series of tests, the MMA waste fuel was artifically spiked with chlorinated POHCs, namely carbon tetrachloride (CCl_4), chlorobenzene ($Cl\Phi$), and trichloroethylene (TCE).

Table II summarizes the salient operating conditions of the boiler during the tests. Increases in excess combustion air were generally required during cofiring conditions. Excess O_2 measured by boiler control room meter averaged 3 percent during baseline and was increased to a range of 4 to 6 percent during cofiring. These higher combustion air levels during waste fuel burning were implemented to maintain smoke emissions at a minimum. Despite this measure, several smoke emission episodes occurred during flue gas emissions testing, as noted in Table II.

TABLE II - BOILER OPERATING SUMMARY

Boiler No. 1

Primary and Waste Fuels	No. 6 Oil (Baseline)	No. 6 Oil and Bottoms	No. 6 Oil and Spiked Bottoms
Steam flow, (kg/s) (10^3 lb/hr)	6.8 (54)	7.0 (56)	7.0 (56)
No. 6 oil flow, (ml/s) (gpm)	515 (8.18)	448 (7.12)	362 (5.74)
Waste fuel flow, (ml/s) (gpm)	0	195 (3.10)	249 (3.95)
Total heat input, (MW) million Btu/hr)	21.8 (74.2)	24.0 (82.0)	21.3 (72.7)
Waste fuel heat input (percent of total)	0	21	28
Boiler out O_2 (percent dry)	3.0	3.9	5.4
Number of smoke emission episodes[a]	0	1	8

[a] Number of recorded smoke alarms. Ringelman number $\geq$ 0.6 during smoke alarm.

Table III describes the waste fuel analysis for the major POHCs, the POHC emission levels, and the calculated POHC DREs. Data presented in Table III represent the arithmetic averages of duplicate analysis. All emissions are on a blank corrected basis. Table IV describes the criteria gaseous emissions measured for each test. Data in Table IV represent the average measured values for each test series.[4]

Boiler Number Two

Industrial boiler number two was a balanced draft Babcock and Wilcox watertube boiler with a rated steam capacity of 7.6 kg/s (60,000 lb/hr) of saturated steam at 1.4 MPa (200 psig). This boiler, orginially designed for coal burning, was equipped with two B&W circular burners arranged in two levels, each capable of burning No. 6 oil, No. 2 oil, natural gas, or propane.

The boiler was normally cofired with a purge thinner originating from the purging of paint spray guns. The waste solvent was introduced through a separate pressure-atomized y-jet B&W oil gun near the center of the lower burner. The firing rate of the purge thinner was generally limited to approximately 31 ml/s (30 gph) and automatically shut off when the boiler steam load fell below 3.8 kg/s (30,000 lb/hr). For this test, the cutoff point was lowered to 2.5 kg/s (20,000 lb/hr).

The test program consisted of four tests: one baseline and three cofiring tests. The baseline fuel was No. 6 fuel oil. During the cofiring test, the fuel oil was supplemented with purge thinners. The purge thinner was spiked with carbon tetrachloride (CCl_4), trichloroethylene (TCE), and chlorbenzene (Cl_Φ).

Some problems were experienced with feeding and operation of the boiler. The chlorinated compounds did not mix well with the thinner and their concentration tended to increase over time. During the final day of testing, the concentration of the chlorinated compounds was reduced as additional

TABLE III - POHC INPUTS, EMISSIONS, AND DREs

Boiler No. 1

	NO. 6 OIL AND BOTTOMS			NO. 6 OIL AND SPIKED BOTTOMS		
	Input (mg/ml)	Emissions (μg/s)	DRE (%)	Input (mg/ml)	Emissions (μg/s)	DRE (%)
Carbon Tetrachloride (CCl_4)	ND	77	NA	28.5	22.7	99.9997
Chlorobenzene (Cl_Φ)	ND	2.8	NA	16.2	74.3	99.9981
Trichloroethylene (TCE)	ND	38	NA	29.0	74.3	99.9990
Methyl Methacrylate (MMA)	34.1	220	99.997	40.1	1925	99.976

ND - Not Detected (Concentration Is Below Detection Limit)
NA - DRE Not Applicable (No POHC Input)

TABLE IV - CRITERIA GASEOUS AND PARTICULATE EMISSIONS

Boiler No. 1

STACK EMISSION (Units)	NO. 6 OIL	NO. 6 OIL AND BOTTOMS	NO. 6 OIL AND SPIKED BOTTOMS
O_2 (%)	3.8	5.5	6.9
CO_2 (%)	12.3	11.6	10.6
CO (ppm)	87	97	134
(ng/J)	30	33	46
NO (ppm)	278	378	428
(ng/J as NO_2)	156	212	241
SO_2 (ppm)	276	196	190
(ng/J)	216	153	149
HC (ppm) (C_1 to C_6)	37	142	91
(ng/J as C_1)	7.1	28	17.7
HCl (ng/J)	7.0	3.5	329
(lb/hr)	(1.2)	(0.8)	(55.4)
Particulate (ng/J)	13.9	13.6	16.4
Mass (lb/hr)	(2.56)	(2.56)	(2.81)

thinner was added to the mixing tank to maintain uninterrupted flow to the boiler. Shortly after the third test, the boiler was shut down due to a coked oil gun. The gun was cleaned and reinserted further into the boiler. During the final day of testing, the other oil gun exhibited the same problem and shut down the boiler. The boiler was brought back online after cleaning and repositioning the gun further into the boiler. After both guns were inserted further into the boiler, the problems were corrected.

Table V describes the operating conditions of and the non-POHC emissions from the boiler during the tests. The purge thinner ranged from 9 to 10

percent of the total heat input. The high excess air levels are typical of the operation of this boiler, but are likely to be well above design specifications.

Table VI summarizes the POHC content of the waste and spiked feeds. Toluene was the primary POHC material in the thinner. Table VII presents the POHC inputs, POHC emissions, and calculated DRE's achieved during the tests.

Boiler Number Three

Boiler number three was a Foster Wheeler, Type AG252, forced draft, bent tube boiler, commissioned in 1960 and was used under normal operation to provide steam for plant processing needs. At peak load it could deliver 62,000 pounds per hour of saturated 175 psig steam. The boiler's rated heat input

TABLE V - BOILER OPERATING CONDITIONS AND NON-POHC EMISSIONS

Boiler No. 2

	BASELINE	COFIRE
Steam Flow (kg/s) (1000 lb/hr)	4.0 (32)	4.0 (32)
Air Flow (kg/s) (1000 lb/hr	4.9 (39)	5.1 (40)
Excess Air (%)	66	62
Oil Flow (l/s) (gph)	0.251 (239)	0.215 (204)
Thinner Flow (l/sec) (gph)	--	0.031 30
O_2 (%)	8.6	8.4
CO_2 (%)	9.0	8.9
CO (ppm)	135	124
NO (ppm) (ng/J as NO_2)	328 271	272 245
Particulate Mass g/dscm) (ng/J)	0.0176 7.61	0.0868 40.8
HCl (ng/J) (lb/hr)	36.8 (2.87)	287.3 (22.73)

TABLE VI - VOLATILE ORGANIC COMPOSITION OF THINNER (Grams Per Liter)

Boiler No. 2

COMPOUND	UNSPIKED THINNER	SPIKED THINNER
RCRA Appendix VIII		
Carbon tetrachloride*	<1	27.5
Chlorobenzene*	<1	4.0
Trichloroethylene*	<1	41.2
Toluene	13.75	8.8

*Added to the thinner for purposes of this test.

TABLE VII - POHC INPUTS, EMISSIONS, AND DREs

Boiler No. 2

	BASELINE	COFIRE		
	Emissions (μg/s)	Input (μg/s)	Emissions (μg/s)	DRE (%)
CCl_4	29.6	806,000	216.0	99.995
Cl_Φ	7.4	110,100	14.3	99.987
TCE	102	1,098,333	71.8	99.996
Toluene	128	269,667	154.6	99.95

capacity was 85.73 M Btu/hr. The boiler contained two Peabody circular burners with steam atomizing tips. The boiler was originally designed to fire natural gas or fuel oil. However, modifications had been made so that the boiler could fire waste fuel gas with small amounts of organic liquid waste. The waste fuel gas consisted largely of methane while the typical liquid waste feed was a mixture of nitrobenzene, aniline, and benzene. For the hazardous waste material firing test, a "spike" of carbon tetrachloride, trichloroethylene, monochlorobenzene, and toluene was added to the liquid waste mixture.

The boiler controls had been modified to achieve a "staged" combustion affect during periods of liquid waste firing. The staged combustion was employed as a means to minimize NO_x emissions when the high nitrogen content

liquid wastes were burned. To achieve this staging, the air register to the lower of the two vertical burners was partially closed. The restriction of the airflow to the bottom burner increased the pressure in the windbox and, therefore, the inflow rate to the upper burner. The O_2 trim control, which responded to excess O_2 in the flue gas, maintained the total airflow to the boiler at the level required to meet stoichiometric and excess air requirements for combustion. The airflow imbalance between the upper and lower burner did not significantly affect heat release from the fuel. It served only to promote oxygen lean combustion in the lower flame zone, where the bulk of the nitrogenous liquid waste was combusted, and O_2 rich combustion in the upper flame zone. A major objective in testing this boiler was to determine if boiler modification for NO_x control would produce operating conditions that are unfavorable for waste compound destruction.

Table VIII describes the boiler operating conditions that existed and the non-POHC emissions measured during the staged combustion tests. The background tests refer to tests when only natural gas and waste fuel gas were burned. No liquid waste was burned during the background tests. All data are averages of three independent test runs.

Table IX summarizes input and output concentrations and DREs of the various POHCs during the liquid waste test runs. The average waste feed rate to the boiler during the liquid waste tests was 0.598 gallons per minute.[6]

Boiler Number Four

Boiler number four was a North American Model 3200X packaged, fire-tube boiler. At normal rating, the boiler produced 6900 pounds per hour of 150 psig steam. The maximum heat input to the boiler was 8.4 million Btu/hr. The single burner was a North American Group 4 oil burner. As is typical of such firetube designs, the boiler featured a relatively high combustion temperature and a relatively short gas retention time.

The boiler normally operated intermittently to satisfy the demands of a cyclic solvent recovery process. The boiler was designed to fire either gas or oil but normally burned natural gas. During the waste material firing test program, the boiler burned a fuel that consisted of approximately 98 percent toluene and from 0.5 to 2.0 percent chlorinated POHC materials. To provide controllable test conditions, the test boiler was operated at steady state for 10 to 12 hours per day by venting steam when necessary. Each morning before testing began, the boiler was fired on natural gas for at least one-half hour to heat up all combustion gas contact surfaces to minimize corrosion caused by the high chlorine content of the test fuel.

Table X describes the boiler operating conditions and non-POHC emissions recorded during the tests that are described here. No background tests were required since the fuel was composed entirely of POHC materials. Table X does, however, describe test runs conducted at full and half load conditions, to examine the impact of load variation on POHC DRE.

Table XI summarizes the POHC inputs, emissions, and DREs observed during the boiler tests. POHC DREs, with the exception of monochlorobenzene, were generally above the 99.99 percent level.[7]

TABLE VIII - BOILER OPERATING CONDITIONS AND NON-POHC EMISSIONS

Boiler No. 3

	BACKGROUND	LIQUID WASTE
Steam Production Rate (1000 lb/hr)	39.8	40.3
Fuel Gas Flow (lb/hr)	2065.2	1882.0
Liquid Waste Flow (lb/hr)	0	362.8
O_2 (% by volume)	2.40	2.59
NO_x (ppmv)	80	420
CO (ppmv)	48	180
CO_2 (% by volume)	11.09	10.43
Total HC (ppmv)	5.5	6.4
HCl (mg/m^3)	5.2	605.5

TABLE IX - POHC INPUTS, EMISSIONS, AND DRE's

Boiler No. 3

POHC	WASTE INPUT (Wt. %)	STACK CONCENTRATION ($\mu g/m^3$)	POHC DRE (%)
Benzene	1.67	64.07	99.97
Toluene	3.40	8.45	99.997
CCl_4	1.70	4.90	99.997
Cl_ϕ	3.17	14.87	99.998
TCE	1.67	1.07	99.999
Aniline	2.63	4.93	99.998
Nitrobenzene	82.93	33.97	99.999

CONCLUSIONS

For all the boiler tests described here, the calculated waste destruction efficiencies were in the vicinity of that required under the RCRA incinerator regulations. Similar boilers, if operated under similar conditions,

with similar wastes and at equivalent waste concentration to those used during these tests, should achieve similar waste compound destruction efficiencies.

TABLE X - BOILER OPERATING CONDITIONS AND NON-POHC EMISSIONS

Boiler No. 4

	Full Load	Half Load
Steam Production Rate (1000 lb/hr)	6.9	3.5
Excess Air (%)	37.7	37.8
CO_2 (%)	14.1	12.1
O_2 (%)	4.0	5.9
CO (ppm)	142	108
NO_x (ppm)	NR	172*
Total HC (ppm)	ND	1.5
HCl (mg/sec)	692	575

*Average of only 2 points.
NR - No Recorded
ND - Not Detected

TABLE XI - POHC INPUTS, EMISSIONS, AND DREs

Boiler No. 4

	Full Load			Half Load		
	Input (mg/sec)	Emission (μg/sec)	DRE (%)	Input (mg/sec)	Emission (μg/sec)	DRE (%)
CCl_4	479	5.3	99.9989	308	6.6	99.9979
TCE	532	0.8	99.9998	298	0.33	99.9989
Cl_Φ	204	110	99.9461	108	52	99.9519
Toluene	56,100	477	99.9991	28700	97	99.9997

It must be noted, however, that during these waste tests, the boilers were not operated in a normal mode. Boiler parameters such as load and excess air rates were held constant during each test run to ensure uniform conditions over the required three-hour sampling period. During "upset" conditions such as smoke incidents or carbon monoxide excursions, the sampling probes were pulled from the stack until steady state conditions were regained. Boilers, of course, generally operate in a load demand mode. This test program provides little information on the impact of load variation and transitions between load points on POHC DREs.

In addition, physical conditions of waste feed and boiler operation were not necessarily representative of "typical" operations. Boiler number four was "tuned" by the manufacturer just prior to the test to ascertain that the boiler was operating within specifications. At boiler number three, the liquid waste was decanted prior to introduction to the boiler in order to facilitate pumpability and provide constant waste conditions over the test program.

The data on the emissions of products of incomplete combustion (PICs) are still being analyzed for these boiler tests. Although these emissions were measured, the data is not yet in a form adequate for presentation.

Emissions of metals must also be measured from boilers burning waste materials. Metal emissions, particularly from boilers burning organometallics or pesticides, could impose more severe risks than organic emissions.

On balance, well operated boilers appear to hold considerable promise for hazardous waste material destruction. The opportunity cost savings from not having to construct a separate waste disposal facility are considerable and significant fuel cost savings could be provided by firing high heating value fuels. The nature of boiler function imposes some conditions that will bias these operations toward achievement of high DREs. Boilers must maintain steam production temperatures. Boilers cannot accept large quantities of the difficult to destroy chlorinated compounds due to the highly corrosive effect of the resultant hydrochloric acid (HCl) on boiler internal components.

FURTHER WORK

The boiler tests described here are components of broader programs being conducted by EPA. Other such source tests have been conducted and additional tests of boilers and other industrial processes are planned. Also tests of such processes will be conducted under non-steady state conditions to determine which conditions constitute an acceptable operating envelope for those processes when hazardous waste materials are fired.

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